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(54) TREATING METHOD FOR (METH)ACRYLIC POLYMER

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a treating method for a (meth)acrylic polymer produced by utilizing the atom transfer radical polymerization.

SOLUTION: The treating method, which is for the (meth)acrylic polymer manufactured by utilizing the atom transfer radical polymerization using a transition metal complex as the polymerization catalyst, is characterized by heating the polymer in the presence of an antioxidant at 120–250° C, preferably 140–220° C. The antioxidant is preferably an inhibitor of radical chain reaction, concretely, a phenolic antioxidant and/or an amine antioxidant. Heating the (meth)acrylic polymer in the presence of the antioxidant is preferably conducted in the copresence of a synthetic hydrotalcite, aluminum silicate or magnesium oxide.

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CLAIMS

[Claim(s)]

[Claim 1] The art of the acrylic polymer which makes a transition metal complex a polymerization catalyst, is the art of the acrylic polymer manufactured using an atomic migration radical polymerization (meta), and is characterized by heating an acrylic (meta) polymer at 120-250 degrees C under existence of an antioxidant (meta).

[Claim 2] The art of the acrylic polymer which makes a transition metal complex a polymerization catalyst, is the art of the acrylic polymer manufactured using an atomic migration radical polymerization (meta), and is characterized by heating an acrylic (meta) polymer at 140-220 degrees C under existence of an antioxidant (meta).

[Claim 3] The art of the acrylic polymer according to claim 1 or 2 (meta) whose anti-oxidant is radical chain inhibitor.

[Claim 4] The art of the acrylic polymer according to claim 1 or 2 (meta) whose antioxidants are a phenolic antioxidant and/or an amine system antioxidant.

[Claim 5] An acrylic polymer, aliphatic hydrocarbon and aromatic hydrocarbon, with a carbon numbers of five or more aliphatic series ester. (Meta) After mixing one sort of solvents chosen from the group which consists of the aliphatic series ether, this mixture is heated under existence of an antioxidant. And by centrifugal separation, natural sedimentation, or filtration after that (Meta) The art of an acrylic (meta) polymer given in any 1 term of claims 1-4 characterized by separating an acrylic polymer and a transition-metals compound.

[Claim 6] (Meta) The art of an acrylic (meta) polymer given in any 1 term of claims 1-5 which heat under existence of an antioxidant and are characterized by separating an acrylic (meta) polymer and a transition-metals compound by centrifugal separation, natural sedimentation, or filtration after that after mixing two or more sorts of solvents chosen from an acrylic polymer, aliphatic hydrocarbon and aromatic hydrocarbon, with a carbon numbers of five or more aliphatic series ester, and the group that consists of the aliphatic series ether.

[Claim 7] (Meta) The art of an acrylic (meta) polymer given in any 1 term of claims 1-6 characterized by making one sort or two sorts or more of adsorbents chosen from the group which consists of a synthetic hydrotalcite, aluminum silicate, and a magnesium oxide live together in case an acrylic polymer is heated under existence of an antioxidant.

[Claim 8] (Meta) The art of an acrylic (meta) polymer given in any 1 term of claims 1-7 characterized by heating an acrylic polymer, making oxygen / nitrogen mixed gas contact.

[Claim 9] (Meta) The art of an acrylic (meta) polymer given in any 1 term of claims 1-8 characterized by heating an acrylic polymer, making the oxygen / nitrogen mixed gas which has the oxygen atom of a mol 0.1 to 5000 times exist in the gaseous-phase section, and contacting it to oxygen / nitrogen mixed gas to the total number of mols of the transition metals contained in an acrylic polymer (meta).

[Claim 10] The art of an acrylic (meta) polymer given in any 1 term of claims 5-9 characterized by the specific inductive capacity in 25 degrees C of a solvent being five or less.

[Claim 11] The art of an acrylic (meta) polymer given in any 1 term of claims 5-9 characterized by being what chosen from the group which a solvent becomes from n-hexane, a cyclohexane, a methylcyclohexane, ethylcyclohexane, toluene, a xylene, butyl acetate, and diethyl ether.

[Claim 12] The art of an acrylic (meta) polymer given in any 1 term of claims 1-11 which make a transition metal complex a polymerization catalyst and are characterized by heating the acrylic polymer manufactured using an atomic migration radical polymerization (meta) under reduced pressure under existence of an antioxidant.

[Claim 13] (Meta) An art given in any 1 term of claims 1-12 characterized by performing dehalogenation of an acrylic polymer.

[Claim 14] An art given in any 1 term of claims 1-13 to which number average molecular weight of the acrylic (meta) polymer after processing is characterized by or more 1000 being 100000 or less.

[Claim 15] An art given in any 1 term of claims 1-14 to which the molecular weight distribution (weight average molecular weight/number average molecular weight) of the acrylic (meta) polymer after processing are characterized by or more 1.05 being 1.50 or less.

[Claim 16] The acrylic polymer obtained from claim 1 by the art given in 15 any 1 terms (meta).

[Claim 17] The acrylic ester system polymer obtained from claim 1 by the art given in 15 any 1 terms.

[Claim 18] The hydrosilylation reactivity constituent containing an acrylic polymer according to claim 16 or 17 (meta).

[Claim 19] The manufacture approach of the acrylic polymer characterized by carrying out the art of a publication to 15 any 1 terms from claim 1 (meta).

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] the process at which this invention removes from a polymer the transition metal complex which is atomic migration radical polymerization catalyst in more detail about the art of an acrylic (meta) polymer, or a polymerization — it is related with the process described from a halogen radical in the living body.

[0002]

[Description of the Prior Art] A hydrosilylation reaction is used for functional-group conversion, crosslinking reaction, etc., and is one of the industrial very useful reactions. For example, it is known that the polymer which has a cross-linking silyl radical at the end giving the hardened material which carried out bridge formation hardening and was [endurance / thermal resistance,] excellent, and by masking the hydrosilyl radical content compound which has a cross-linking silyl radical react to the polymer which has an alkanyl radical as a functional group at the end of a chain uses a hydrosilyl radical content compound as a curing agent. Although these hydrosilylation reactions advance by heating, a hydrosilylation catalyst is added in order to advance a reaction more quickly. As such a hydrosilylation catalyst, transition metal catalysts, such as radical initiators, such as organic peroxide and an azo compound, and a platinum catalyst, are mentioned. If transition metal catalysts, such as a platinum catalyst, are used especially, it is known that hydrosilylation can be quickly advanced with the catalyst of a minute amount.

[0003] On the other hand, generally the living polymerization method is learned as a precision synthesis method of a polymer. It not only says that control of molecular weight and molecular weight distribution is possible, but a polymer with clear end structure is obtained by living polymerization. Therefore, living polymerization is mentioned as one of the effective approaches of introducing a functional group into a polymer end. Recently, also in the radical polymerization, the polymerization system in which living polymerization is possible is found out, and research of a living radical polymerization is done actively. The narrow (meta) acrylic polymer of molecular weight distribution is obtained by using especially an atomic migration radical polymerization. The polymerization system which makes a catalyst the metal complex which uses an initiator, the 8th group of the periodic table, nine groups, ten groups, or 11 group element as a central metal for an organic halogenide or a halogenation sulfonyl compound as an example of an atomic migration radical polymerization is mentioned. (see Matyjaszewski et al., J.Am.Chem.Soc.1995, 117 and 5614, Macromolecules 1995, 28 and 7901, Science 1996, 272 and 866 or Sawamoto et al., Macromolecules 1995, 28 and 1721).

[0004]

[Problem(s) to be Solved by the Invention] However, since the transition metal complex which is a polymerization catalyst remains in the acrylic polymer manufactured by the atomic migration radical polymerization (meta), problems, such as coloring of a polymer, effect on a physical-properties side, and environmental safety, arise. For example, in the acrylic polymer which has an alkanyl radical at the end manufactured using the atomic migration radical polymerization method

the group which consists of a synthetic hydrotalcite, aluminum silicate, and a magnesium oxide live together (claim 7). Moreover, in this invention, it is desirable to heat an acrylic (meta) polymer, making oxygen / nitrogen mixed gas contact (claim 8). Moreover, it sets to this invention, (meta) it is desirable to heat an acrylic polymer, making the oxygen / nitrogen mixed gas which has the oxygen atom of a mol 0.1 to 5000 times exist in the gaseous-phase section to the total number of mols of the transition metals contained in an acrylic polymer, and making oxygen / nitrogen mixed gas contact (claim 9). (meta)

[0013] Moreover, in this invention, it is desirable that the specific inductive capacity in 25 degrees C of a solvent is five or less (claim 10). Moreover, it sets to this invention, It is desirable that it is what is chosen from the group which a solvent becomes from n-hexane, a cyclohexane, a methylcyclohexane, ethylcyclohexane, toluene, a xylene, butyl acetate, and diethyl ether (claim 11). Moreover, in this invention, it is desirable to heat the acrylic polymer which makes a transition metal complex a polymerization catalyst and is manufactured using an atomic migration radical polymerization (meta) under reduced pressure under existence of an antioxidant (claim 12).

[0014] Moreover, in this invention, it is desirable to perform dehalogenation of an acrylic (meta) polymer (claim 13). Moreover, in this invention, it is desirable that the number average molecular weight of the acrylic (meta) polymer after processing is 100000 or less [1000 or more] (claim 14). Moreover, in this invention, it is desirable that the molecular weight distribution (weight average molecular weight/number average molecular weight) of the acrylic (meta) polymer after processing are 1.50 or less [1.05 or more] (claim 15).

[0015] Moreover, this invention relates to the art of the acrylic (meta) polymer for obtaining the acrylic polymer which is one component of a hydrosilylation reactivity constituent (meta) (claims 16-18). Moreover, this invention relates to the manufacture approach of the acrylic polymer characterized by performing the above-mentioned art (meta) (claim 19).

[0016]

[Embodiment of the Invention] This invention is the art of the acrylic polymer which makes a transition metal complex a polymerization catalyst, is the art of the acrylic polymer manufactured using an atomic migration radical polymerization (meta), and is characterized by heating an acrylic (meta) polymer at 120-250 degrees C under existence of an antioxidant (meta).

[0017] An atomic migration radical polymerization is described first. The atomic migration radical polymerization in this invention is one of the living radical polymerizations, and is the approach of carrying out the radical polymerization of the acrylic (meta) monomer by making into a catalyst the metal complex which uses an initiator an organic halogenide or a halogenation sulfonyl compound, and uses transition metals as a central metal.

[0018] In this atomic migration radical polymerization, an organic halogenide especially the organic halogenide (for example, the carbonyl compound which has a halogen in an alpha position and the compound which has a halogen in the benzyl position) which has reactant high carbon-halogen association, or a halogenation sulfonyl compound is used as an initiator.

[0019] By performing the atomic migration radical polymerization of an acrylic (meta) monomer by making an organic halogenide or a halogenation sulfonyl compound into an initiator, the acrylic polymer which has the end structure shown in a general formula (1) (meta) is obtained.

-C(R1)X2(XX) (1)

(R1 and R2 show among a formula the radical combined with the ethylene nature partial saturation radical of an acrylic (meta) monomer.) X shows chlorine, a bromine, or iodine. The organic halogenide or halogenation sulfonyl compound having the specific reactant functional group which does not start a polymerization as an initiator of an atomic migration radical polymerization with the functional group which starts a polymerization can also be used. In such a case, the acrylic polymer which has the end structure which shows a specific reactant functional group in a general formula (1) at the principal chain end of another side at one principal chain end (meta) is obtained. As such a specific reactant functional group, an alkanyl radical, a cross-linking silyl radical, hydroxyl, an epoxy group, the amino group, an amide group, etc. are mentioned. Other suitable functional groups can be introduced into an acrylic (meta)

(meta), in order that a residual catalyst etc. might work as catalyst poison of a hydrosilylation reaction, the hydrosilylation reaction was checked, and the problem that many expensive hydrosilylation catalysts were needed arose.

[0005] this invention persons found out that hydrosilylation activity improved by contacting the acrylic polymer obtained by the atomic migration radical polymerization (meta) to an adsorbent, and refining it (JP.11-193307(A)). However, the rise of the purification cost by the load to the environment there is a much amount of the adsorbent used in that case, and according to abandonment and the adsorbent etc. may arise as a problem. Furthermore, since whenever [sufficient in low temperature treatment 120 degrees C or less purification] is not obtained or a lot of adsorbents are needed, as processing temperature, an elevated temperature is desirable. Moreover, the acrylic polymer manufactured according to an atomic migration radical polymerization (meta) has table radicals, such as a halogen, at the end. A halogen radical causes coloring or causes problems, such as deterioration of the quality of the product by generating of a free acid etc., and corrosion of a facility. As a dehalogenation method, although indicated, for example (JP.2000-344831(A)), there is a problem of a halogenation processing agent's being required and processing conditions being limited. Moreover, the thermal stability of the polymer itself may be unable to be held depending on purification temperature. (Meta) Generally the acrylic polymer is excellent in thermal resistance, and high temperature processing is possible for it as compared with other polymers. However, the acrylic polymer manufactured according to an atomic migration radical polymerization (meta) has the polymerization catalyst which remains in a polymer, and the inclination to deteriorate under the effect of a halogen radical etc. That is, if it heats in the cases, such as a purification process, a dehalogenation process, and a solvent removal process, a polymerization catalyst, a halogen radical, etc. will serve as a catalyst, and thermal degradation of dimerization (the so-called molecular-weight jump) of a polymer etc. will start in many cases.

[0006] This invention offers the art in which heating-at-high-temperature processing is possible, controlling thermal degradation of an acrylic (meta) polymer.

[0007]

[Means for Solving the Problem] this invention persons completed this invention, as a result of examining wholeheartedly the art in which heating-at-high-temperature processing is possible, controlling thermal degradation about the acrylic (meta) polymer manufactured by the atomic migration radical polymerization.

[0008] That is, this invention relates to the art of the acrylic polymer which makes a transition metal complex a polymerization catalyst, is the art of the acrylic polymer manufactured using an atomic migration radical polymerization (meta), and is characterized by heating an acrylic (meta) polymer at 120-250 degrees C under existence of an antioxidant (meta) (claim 1).

[0009] It is desirable to heat an acrylic (meta) polymer at 140-220 degrees C under existence of an antioxidant in this invention (claim 2). Moreover, in this invention, it is more desirable that it is a phenolic antioxidant and/or an amine system anti-oxidant that an anti-oxidant is radical chain inhibitor preferably (claim 3) (claim 4).

[0010] Moreover, in this invention, after mixing one sort of solvents chosen from an acrylic (meta) polymer, aliphatic hydrocarbon and aromatic hydrocarbon, with a carbon numbers of five or more aliphatic series ester, and the group that consists of the aliphatic series ether, it is desirable to heat this mixture under existence of an antioxidant and to separate an acrylic (meta) polymer and a transition-metals compound by centrifugal separation, natural sedimentation, or filtration after that (claim 5).

[0011] Moreover, in this invention, after mixing two or more sorts of solvents chosen from an acrylic (meta) polymer, aliphatic hydrocarbon and aromatic hydrocarbon, with a carbon numbers of five or more aliphatic series ester, and the group that consists of the aliphatic series ether, it is desirable to heat under existence of an antioxidant and to separate an acrylic (meta) polymer and a transition-metals compound by centrifugal separation, natural sedimentation, or filtration after that (claim 6).

[0012] Moreover, in this invention, in case an acrylic (meta) polymer is heated under existence of an antioxidant, it is desirable to make one sort or two sorts or more of adsorbents chosen from

polymer by passing through a single step or several steps of reactions using the reactivity of these reactant functional groups.

[0020] What has the structure which it is not limited as an organic halogenide which has an alkanyl radical, for example, is shown in a general formula (2) is illustrated.

R6R7C(X)-R8-R9-C(R5)-CH2 (2)
 the inside of a formula, and R5 — hydrogen or a methyl group, and R6 and R7 — hydrogen — The univalent alkyl group of carbon numbers 1-20, an aryl group, an aralkyl or the thing mutually connected in the other end, and R8 [or] — C(O) — (ester group), —C(O) — (keto radical) or —, m-, p-phenylene group, X in which R9 may include one or more ether linkage by direct coupling or the divalent organic radical of carbon numbers 1-20 as an example of chlorine, a bromine, or the iodine substituents R6 and R7 Hydrogen, a methyl group, an ethyl group, n-propyl group, an isopropyl group, butyl, a pentyl radical, a hexyl group, etc. are mentioned. R6 and R7 may be connected in the other end, and they may form the annular frame.

[0021] What has the structure which it is not limited especially as an organic halogenide which has the above-mentioned cross-linking silyl radical, for example, is shown in a general formula (3) is illustrated.

R6R7C(X)-R8-R9-C(H)(R5)CH2-[Si(R11)2-b(Y)b0]m-Si(R12)3-a(Y)a (3)
 the inside of a formula, and R5, R6, R7, R8, R9 and X — the above — the same — R11 and R12 All The alkyl group of carbon numbers 1-20, an aryl group, an aralkyl radical, Or R3SiO — R' is the univalent hydrocarbon group of carbon numbers 1-20 three R' — being the same — differing — **** — when the Tori ORGANO siloxy radical shown is shown and R11 or two or more R12 exist, they may be the same and may differ. When Y shows a hydroxyl group or a hydroxyl nature machine and two or more Y exists, they may be the same and may differ. a shows 0, 1, 2, or 3, and b shows 0, 1, 2, or 2 is the integer of 0-19, however, it shall satisfy that it is a+mb=1 — it is not limited especially as an organic halogenide with the above-mentioned hydroxyl, or a halogenation sulfonyl compound, but a thing like the following general formula (4) is illustrated.

[0022] HO-(CH2)n-OC(O)C(H)(R5) (4)
 (Setting at each above-mentioned ceremony, for chlorine, a bromine or iodine, and R, a hydrogen atom or the siloxy group of carbon numbers 1-20, an aryl group, an aralkyl radical, and n are [X] the integer of 1-20) It is not limited especially as an organic halogenide with the above-mentioned amino group, or a halogenation sulfonyl compound, but a thing like the following general formula (5) is illustrated.

H2N-(CH2)n-OC(O)C(H)(R5) (5)
 (Setting at each above-mentioned ceremony, for chlorine, a bromine or iodine, and R, a hydrogen atom or the siloxy group of carbon numbers 1-20, an aryl group, an aralkyl radical, and n are [X] the integer of 1-20) in order to obtain the polymer which has two or more reactant functional groups in 1 intramolecular, it is desirable to use an organic halogenide with two or more start points or a halogenation sulfonyl compound as an initiator.

[0023] Although not limited especially as a transition metal complex used as a polymerization catalyst, it is the metal complex which uses the 7th group of the periodic table, eight groups, nine groups, ten groups, or 11 group element as a central metal preferably. Furthermore, as a desirable thing, the complex of zerovalent copper, univalent copper, a divalent ruthenium, divalent iron, or divalent nickel is mentioned. Especially, a copper complex is desirable, a univalent copper compound is illustrated concretely — if it becomes — a cuprous chloride and bromination — they are the first copper, a cuprous iodide, a cuprous cyanide, a cuprous oxide, the first copper of perchloric acid, etc. When using a copper compound, in order to raise catalytic activity, polyamine, such as 2,2'-bipyridyl or its derivative, 1,10-phenanthroline, its derivative or tetramethylethylenediamine, pentamethyl diethylenetriamine, or a hexa methyl triis (2-aminoethyl) amine, etc. is added as a ligand.

[0024] There is especially no constraint as an acrylic monomer used in this polymerization (meta). For example, (meta), an acrylic acid, a methyl acrylate (meta), an ethyl acrylate (meta), Acrylic-acid-n-propyl, acrylic-acid-(meta) isopropyl, (Meta) Acrylic-acid-n-butyl, isobutyl

acrylate (meta), (Meta) Acrylic-acid-tert-butyl, acrylic-acid (meta)-n-pentyl, (Meta) Acrylic-acid-n-hexyl, acrylic-acid (meta) cyclohexyl, (Meta) Acrylic-acid-n-heptyl, acrylic-acid (meta)-n-octyl, (Meta) 2-ethylhexyl acrylate, acrylic-acid (meta) nonyl, (Meta) Acrylic-acid DESHIRU, acrylic-acid (meta) dodecyl, acrylic-acid (meta) phenyl, (Meta) Acrylic-acid tolyl, acrylic-acid (meta) benzyl, acrylic-acid (meta)-2-methoxy ethyl, (Meta) Acrylic-acid-3-methoxy butyl, acrylic-acid (meta)-2-hydroxyethyl, (Meta) (Meta) 2-hydroxypropyl acrylate, acrylic-acid (meta) stearyl, metaglycidyl acrylate (meta), acrylic-acid (meta) 2-aminoethyl, gamma-(methacryloyl oxypropyl) trimethoxysilane, etc. are mentioned. These may be used independently, and even if it carries out copolymerization of the plurality, they are not cared about. Especially, the styrene system monomer from physical properties etc. and (meta) acrylic-acid system monomer of a product are desirable. More preferably, it is an acrylic ester monomer and a methacrylic ester monomer, is an acrylic ester monomer especially preferably, and is butyl acrylate still more preferably. In this invention, it is desirable other monomers, copolymerization, and that may carry out block copolymerization further and these desirable monomers are contained 40% or more by the weight ratio in these desirable monomers in that case. In addition, an acrylic acid (meta) expresses an acrylic acid and/or, a methacrylic acid with the above-mentioned transcription.

[0025] A polymerization reaction can also be performed in various kinds of solvents, although a non-solvent is also possible. It is not limited especially as a class of solvent. For example, hydrocarbon system solvent; diethylether, such as benzene and toluene, Ether system solvents, such as a tetrahydrofuran, diphenyl ether, an anisole, and dimethoxybenzene; A methylene chloride, Halogenated hydrocarbon system solvents, such as chloroform and a chlorobenzene; An acetone, Ketone solvent, such as a methyl ethyl ketone and methyl isobutyl ketone; A methanol, Ethanol, Propanol, Isopropanol, n-butyl alcohol, Alcoholic solvent, such as tert-butyl alcohol; An acetonitrile, Nitrile system solvents, such as propionitrile and a benzonitrile; Ethyl acetate, Ester solvent, such as butyl acetate; amide system solvents, such as carbonate system solvent; N,N-dimethylformamide, such as ethylene carbonate and propylene carbonate, and N,N-dimethylacetamide, etc. are mentioned. Even when these are independent, they are good, and they may use two or more sorts together.

[0026] Although limitation is not carried out, a polymerization can be performed in 0-200 degrees C, and the range of it is room temperature -150 degrees C preferably.

[0027] Next, the acrylic polymer in this invention (meta) is described. The acrylic polymer in this invention (meta) means the polymer whose 40% or more of the total number of mols of a monomer used for the polymerization reaction is an acrylic (meta) monomer.

[0028] (Meta) Although especially an acrylic polymer is not limited, it is preferably manufactured according to the atomic migration radical polymerization of an acrylic (meta) monomer. It is not limited especially as such (meta) an acrylic monomer, but what was already illustrated can be used. As an acrylic monomer in this invention (meta), an acrylic ester monomer and a methacrylic ester monomer can be raised, for example. These (meta) acrylic monomers may be used independently, and even if it carries out copolymerization of the plurality, they are not cared about. An acrylic ester monomer and a methacrylic ester monomer are desirable, especially a desirable thing is an acrylic ester monomer, and butyl acrylate is still more desirable. In this invention, it is desirable other monomers, copolymerization, and that may carry out block copolymerization further and these desirable monomers are contained 40% or more by the weight ratio in these desirable monomers in that case.

[0029] (Meta) Although especially the molecular weight distribution of an acrylic polymer, i.e., the ratio of the weight average molecular weight measured with gel permeation chromatography and number average molecular weight, are not limited, it is less than 1.8 preferably and is 1.5 or less more preferably.

[0030] (Meta) Although especially a limit does not have the number average molecular weight of an acrylic polymer, the range of 500-1,000,000 is desirable, and 1000-100,000 are still more desirable. If it becomes high too much conversely, handling will become [the original property of an acrylic polymer] will be hard to be discovered if molecular weight becomes low too much (meta) difficult.

[0031] (Meta) The acrylic polymer may have the reactant functional group in intramolecular.

alkenyl radical of diene series. When a big difference is in the reactivity of two alkenyl radicals, the addition of the diene series to a polymerization growth end. Although the equivalent (one mol of diene series [as opposed to / Namely, / one mol of polymerization growth ends]) or small excessive-amount extent is sufficient. Since both two alkenyl radicals react and polymerization ends carry out coupling when there is no difference not much, or the reactivity of two alkenyl radicals is equal. The addition of diene series is 5 or more times especially preferably 3 or more times still more preferably 1.5 or more times preferably [it is desirable that it is an excessive amount to a polymer growth end, and].

[0041] Next (meta), the art of an acrylic polymer is described. The processing in this invention mainly means the following three. (1) It is the isolation (purification) process of a polymer and include removal of a residual monomer, a polymerization solvent, and residual diene series, and removal of a residual polymerization catalyst. (2) It is a polymer denaturation process and they are halogen radical removal, functional-group conversion, etc. (3) Solvent removal used at each process.

[0042] The acrylic (meta) polymers obtained by the above-mentioned atomic migration radical polymerization approach are a polymerization solvent, a residual monomer, residual diene series, and the mixture of a transition metal complex, and need to remove these from a polymer. In it, a polymerization solvent, a residual monomer, and residual diene series are volatile liquids fundamentally [a certain thing], and can separate the difference of the boiling point from a polymer in the various usual evaporation actuation. Under the present circumstances, generally a polymer is heated. However, if heating at high temperature is carried out under the transition metal complex existence which is a polymerization catalyst, molecular weight increase will tend to take place. Moreover, even if the transition metal complex and transition metals which are polymerization catalysts generally had high compatibility with a polymer and it carried out solid-liquid-separation actuation as it was, a lot of transition metals have dissolved in the polymer. Dissolved transition metals are set to one of the causes, such as catalyst poison of coloring and a hydrolysis reaction, and a storage stability fall, in many cases.

[0043] After mixing the polymer obtained by the atomic migration radical polymerization with one sort of solvents chosen from the group which becomes the bottom of existence of an antioxidant from with a carbon numbers of five or more aliphatic series ester and the aliphatic series ether, it can consider as 120-250 degrees C, and an acrylic (meta) polymer and a transition metal complex can be separated centrifugal separation, natural sedimentation, or by filtering after that. As whenever [stoving temperature], 140 degrees C - 220 degrees C are more desirable.

[0044] Although the transition metal complex used for a polymerization shows a certain amount of solubility comparatively to a polar high halogenated hydrocarbon system solvent, ketone solvent, alcoholic solvent, a nitrile system solvent, and an amide system solvent, it becomes almost insoluble conversely with it at polar low aliphatic hydrocarbon, aromatic hydrocarbon, and fatty acid ester. By adding such a low polar solvent to a polymer, and dissolving a polymer, most transition metal complexes are insolubilized, it gets fat, and serves as a solid-state.

[0045] Although a low polar solvent is illustrated below, it is not limited to these solvents. As aliphatic hydrocarbon, toluene, a xylene, etc. are mentioned as for example, n-hexane, n-heptane, n-octane, a methylcyclohexane, ethylcyclohexane, and aromatic hydrocarbon. Within limits which a polymer dissolves, these solvents may be used independently, or it may mix and they may be used.

[0046] Although the amount of the solvent used is the 10 to 1000 weight section to the acrylic (meta) polymer 100 weight section, it is usually the 50 - 500 weight section more preferably. Insolubilization and the hypertropy effectiveness are low, and conversely, above the 1000 weight sections, if there is almost no difference in the insolubilization effectiveness and solvent recovery cost is considered, as an actual manufacture process, futility will increase under at 10 weight sections.

[0047] Although hypertropy of the above-mentioned transition metal complex and insolubilization may be performed to the solution of the acrylic polymer which is an end product (meta), you may carry out to the intermediate product for manufacturing a \leftrightarrow (meta) acrylic polymer. For example, when using as an end product the acrylic polymer which has an alkenyl

When it has a reactant functional group in intramolecular, you may exist in any of a side chain or a chain end. Although not limited especially as a reactant functional group, an alkenyl radical, a hydroxyl group, the amino group, a cross-linking silyl radical, a polymerization nature carbon-carbon double bond radical, etc. are mentioned, for example.

[0032] Next, the acrylic polymer which has an alkenyl radical (meta) is described. The acrylic polymer which has an alkenyl radical (meta) can be used as a component of a hydroxyl radical in intramolecular (meta) constructs a bridge by performing a hydroxyl radical reaction, using a hydroxyl radical content compound as a curing agent, and gives a hardened material. Moreover, the acrylic polymer which has a cross-linking functional group (meta) is obtained by carrying out the hydroxyl radical reaction of the hydroxyl compound which has a cross-linking functional group in the acrylic polymer which has an at least 1 alkenyl radical in intramolecular (meta). The acrylic polymer which has an alkenyl radical (meta) can be manufactured using an atomic migration radical polymerization.

[0033] Although especially limitation is not carried out, as for the alkenyl radical in this invention, it is desirable that it is what is expressed with a general formula (6).



(R13 shows hydrogen or the organic radical of carbon numbers 1-20 among a formula.) In a general formula (6), R13 is hydrogen or the organic radical of carbon numbers 1-20. Although not limited especially as an organic radical of carbon numbers 1-20, the alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, and the aralkyl radical of carbon numbers 7-20 are desirable.

[0034] Although an alkenyl radical should just exist in the intramolecular of an acrylic (meta) polymer, since the molecular weight between the points constructing a bridge which has big effect on rubber elasticity can take greatly when especially a rubber-property is required of the hardened material of the hardenability constituent of this invention, as for at least one of an alkenyl radical, it is desirable that it is in the end of a chain. It has all alkenyl radicals at the chain end more preferably.

[0035] Although especially the number of alkenyl radicals is not limited, in order to obtain a hardened material with more high cross-linking, it is averaged and is 1.5 or more pieces more preferably 1.2 or more pieces one or more pieces.

[0036] As the manufacture approach of an acrylic polymer of having an alkenyl radical (meta), a diene series addition method is used suitably. A diene series addition method is characterized by making the compound (henceforth "diene series") which has at least two low alkenyl radicals of polymerization nature react to the acrylic polymer obtained according to the atomic migration radical polymerization of an acrylic (meta) monomer (meta).

[0037] At least two alkenyl radicals of diene series are mutually the same — or you may differ. As an alkenyl radical, end alkenyl radical $[\text{CH}_2=\text{CR}(\text{R}')\text{R}']$ is hydrogen or the organic radical of carbon numbers 1-20, R' is the organic radical of carbon numbers 1-20, it may join together mutually and R and R' may have cyclic structure.] Or internal alkenyl radical $[\text{R}'-\text{CR}(\text{R}')-\text{CR}'-\text{R}']$ is hydrogen or the organic radical of carbon numbers 1-20, R' is the organic radical of carbon numbers 1-20, and two R (or two R') may be mutually the same, and may differ. Among two substituents, R and two substituents [two] of R', any two may join together mutually and they may have cyclic structure.] Although ***** is sufficient, an end alkenyl radical is more desirable. Although R is hydrogen or the organic radical of carbon numbers 1-20, as an organic radical of carbon numbers 1-20, the alkyl group of carbon numbers 1-20, the aryl group of carbon numbers 6-20, and the aralkyl radical of carbon numbers 7-20 are desirable. Especially as R, hydrogen or a methyl group is desirable also in these.

[0038] Moreover, at least two alkenyl radicals may be conjugating among the alkenyl radicals of diene series.

[0039] Although an isoprene, piperylene, a butadiene, a myrcene, 1, 5-hexadiene, 1, 7-OKUTA diene, 1, 9-deca diene, a 4-vinyl-1-cyclohexene, etc. are mentioned as an example of diene series, 1, 5-hexadiene, 1, 7-OKUTA diene, 1, and 9-deca diene is desirable.

[0040] It is necessary to adjust the addition of diene series by the radical reaction nature of the

radical (meta), it is possible to perform insolubilization of a transition metal complex and hypertropy to the solution of the acrylic polymer which has high carbon halogen association of \leftrightarrow reactivity considered as an intermediate product for manufacturing a \leftrightarrow (meta) acrylic polymer (meta), or the acrylic polymer which has \leftrightarrow hydroxyl group (meta) not to mention this polymer.

[0048] Hypertropy of a transition metal complex and insolubilization can be promoted by furthermore processing the acrylic polymer manufactured according to the atomic migration radical polymerization of the acrylic monomer which makes a transition metal complex a polymerization catalyst (meta) (meta) at an elevated temperature in this invention. At an elevated temperature, the Brownian motion of the transition metals in the inside of a solvent becomes active statistically, and hypertropy and insolubilization are promoted.

[0049] Although there is especially no limit about the temperature of hypertropy and insolubilization, generally 0 degrees C - 120-250 degrees C 250 degrees C are the range of 140 degrees C - 220 degrees C more preferably. Although especially constraint does not have the time amount to heat, either, it is 180 - 300 minutes preferably.

[0050] In this invention, although insolubilization of a transition metal complex is attained by adding a low polar solvent, when not heating, the generated solid-state may become what has very small particle diameter, and a great effort is needed for next solid liquid separation in this case. In order to specifically separate a particle in a centrifugal separation method, a big centrifugal force's being needed and a particle piling up in equipment, being easy to generate plugging etc., and becoming the trouble of stable operation is mentioned. A facility will be enlarged, as a result of a lot of filter aids will be needed and filtration velocity's also becoming small also in a filtration method on the other hand, if particle diameter is small. Moreover, how the products which remain in a filter aid being collected, and a technical problem will be held.

[0051] By heating a polymer solution, condensation of the transition metal complex which insolubilized is promoted and solid liquid separation becomes easy. When specifically using a centrifugal separator and using the improvement in stability of operation, and a filter, the miniaturization of the facility accompanying the improvement in filtration velocity, improvement in the product yield by reduction of the amount of filter aids, etc. can be expected.

[0052] There is especially no limit as equipment made to dissolve a polymer in a solvent, for example, a mixing vessel general-purpose in a batch type can be used for a fine mixer etc. with continuous system.

[0053] By carrying out the above actuation, an acrylic polymer with few (meta) impurities can be obtained by the transition metal complex in an acrylic (meta) polymer solution insolubilizing, and separating the solid-state which insolubilized. Although especially the method of concrete solid liquid separation is not restricted, it is desirable to be able to use centrifugal separation, natural sedimentation, or a filtration method in this invention, and to use centrifugal separation and a filtration method. As a type of a centrifugal separator, a separation board type (DERABARU), a decanter, a basket, etc. are selectable suitably. Especially the separation board type that has a high centrifugal force especially is desirable.

[0054] As a filtration method, a filter press, a drum filter, a pressurization nutache, a pressurization folaceous filter, etc. can be used. Moreover, in order to raise filterability, the filter aid represented by diatomaceous earth can be added. As a filter aid, a thing with a mean particle diameter of about 5-100 micrometers is desirable. The acrylic (meta) polymer refined only by evaporating the added solvent can be obtained from the found liquid after filtration.

[0055] An acrylic polymer with few (meta) contents of the transition metal complex which is an impurity can be obtained by performing addition, addition of a polar solvent, heating of a solution, and separation actuation of a transition metal complex in which it insolubilized for the above-mentioned antioxidant. Moreover, in an art given in this invention, the thermal stability of an acrylic (meta) polymer can control increase and quality degradation of a polymer by adding an antioxidant in an acrylic (meta) polymer solution. As for the above-mentioned anti-oxidant, it is desirable that it is what has a function as radical chain inhibitor.

[1] To the hardenability constituent of > this invention, an antioxidant may be added if needed about an antioxidant < antioxidant. An anti-oxidant is not necessarily limited to these, although

the various things which various kinds of things are known, for example, were indicated by the "anti-oxidant handbook" of the Taisei Corp. issue, "degradation, stabilization" (235-242) of the CMC chemistry issue of polymeric materials, etc. are mentioned.

[0056] For example, MARK PEP-38, MARK THE Lynn system antioxidants, such as a thioether system (all are the products made from ADEKAA-gasification study above) of AO-23 grade, Irgafos38 and Irgafos168, and Irgafos-EPQ (all are the Ciba-Geigy Japan make above), etc. are mentioned. Especially, a hindered phenol system compound as shown below is desirable.

[0057] As a hindered phenol system compound, the following can specifically be illustrated. 2, 6-G tert-butyl-4-methyl phenol, 2, 6-G tert-butyl-4-ethylphenol, Monochrome (or JI-Tori) (alpha-methylbenzyl) phenol, 2 and 2'-methylenebis (4 ethyl-6-tert-butylphenol), 2 and 2'-methylenebis (4 methyl-6-tert-butylphenol), 4 and 4'-butyldienebis (3-methyl-6-tert-butylphenol), A 4 and 4'-thio screw (3-methyl-6-tert-butylphenol), 2, 5-G tert-butyl hydroquinone, 2, 5-G tert-amyl hydroquinone, Triethylene glycol-screw - [3-(3-tert-butyl-5-methyl-1-hydroxyphenyl) propionate], A 1,6-hexanediol-screw [3-(3-5-G tert-butyl-4-hydroxyphenyl) propionate], 2, 4-screw -(n-octylthio)-6-(4-hydroxy-3, 5-G tert-butylamino)-1,3,5-triazine, Pentaoxythipty-tetraakis-[3-(3-5-G tert-butyl-4-hydroxyphenyl) propionate], A 2 and 2-thiodiethylene screw [3-(3-5-G tert-butyl-4-hydroxyphenyl) propionate]. Octadecyl-3-(3, 5-G tert-butyl-4-hydroxyphenyl) propionate, N and N'-hexa methylenebis (3, 5-G tert-butyl-4-hydroxyhydroxylamine thinner MAMIDO), 3, 5-G tert-butyl-4-hydroxybenzyl FOSUFONETO-diethyl ester, 1, 3, 5-trimethyl-2, 4, 6-tris (3, 5-G tert-butyl-4-hydroxybenzyl) benzene, Bis(3, 5-G tert-butyl-4-hydroxybenzyl phosphonic acid ethyl) calcium, Tris-(3, 5-G tert-butyl-4-hydroxybenzyl) isocyanate, 2, 4-2, 4-screw -(octylthio) methyl o-cresol, N and N'-bis [-] [3-(3-5-G tert-butyl-4-hydroxyphenyl) propionyl] hydrazine, A triis (2, 4-G tert-butyl-4-hydroxyphenyl) FOSU fight, 2-(5-methyl-2-hydroxyphenyl) benzotriazol, 2-[2-hydroxy-3 and 5-bis(alpha and alpha'-dimethylbenzyl) phenyl]-2H-benzotriazol, 2-(3, 5-G tert-butyl-2-hydroxyphenyl) benzotriazol, 2-(3-t-butyl-5-methyl-2-hydroxyphenyl)-5-chlorobenzotriazol, 2-(3, 5-G tert-amyl-2-hydroxyphenyl) benzotriazol, 2-(2-hydroxy-5-t-octyl phenyl)-Benzotriazol, A condensate with a methyl-3-[3-t-butyl-5-(2-benzotriazol-2-IRU)-4-hydroxyphenyl] propionate-polyethylene glycol (molecular weight 300 [about]), A hydroxyphenyl benzotriazol derivative, a 2-(3, 5-G tert-butyl-4-hydroxybenzyl)-2-m-butyl malonic-acid screw (1, 2, 2, 6, and 6-pentamethyl-4-piperidyl), 2, 4-G tert-butylphenyl - 3, 5-G tert-butyl-4-hydroxybenzoate, etc. are mentioned.

[0058] If it says by the trade name, NOKURAKKU 200, NOKURAKKU M-17, NOKURAKKU SP NOKURAKKU SP-N, NOKURAKKU NS-5, NOKURAKKU NS-6, NOKURAKKU NS-30, NOKURAKKU 300, NOKURAKKU NS-7, NOKURAKKU DAH (all are the products made from the Ouchi Shinko Chemical industry above), MARK AO-30, MARK AO-40 and MARK AO-50, MARK AO-60 and MARK AO-618, MARK AO-635, MARK AO-658, MARK AO-80, MARK AO-15, MARK AO-18, MARK 328, MARK AO-37 (all are the products made from ADEKAAGASU chemistry above), IRGANOX-245, IRGANOX-259, IRGANOX-565, IRGANOX-1010, IRGANOX-1024, IRGANOX-1035, IRGANOX-1076, IRGANOX-1081, IRGANOX-1098, IRGANOX-1222, IRGANOX-1330, IRGANOX-1425WL (all are the Ciba-Geigy Japan make above), Although Sumilizer-GM, Sumilizer-GA-80 (all are the Sumitomo Chemical make above), etc. can be illustrated, it is not limited to these.

[0059] Especially since an antioxidant may be used together with the light stabilizer mentioned later, and may demonstrate the effectiveness further by using together and especially its thermal resistance may improve, it is desirable. Tinuvin C353, tinuvin B75 (all are the Ciba-Geigy Japan make above), etc. which have mixed an anti-oxidant and light stabilizer beforehand may be used.

[0060] As for the amount of the antioxidant used, it is desirable that it is the range of 0.01 - 10 weight section to the acrylic (meta) polymer 100 weight section. There is little effectiveness of an improvement of weatherability under at the 0.01 weight section, and in 5 weight *****, there is no great difference in effectiveness and it is economically disadvantageous for it.

[0061] Furthermore by this invention, the actuation described below enables it to obtain more efficiently very little (meta) acrylic polymer of the content of a transition metal complex.

[2] In use this invention of an adsorbent, it is possible by adding a synthetic hydroxalcite,

continue, and to continue oxidation treatment. Moreover, if the approach of making a polymer solution contacting by aeration before heating in addition to this, the approach of carrying out aeration just before solid liquid separation, etc. are contacted before solid liquid separation, especially the other constraint will not have them.

[0063] What is necessary is just to add in a polymer solution in the idea according to this also in a hydrogen peroxide and a fault sodium carbonate, the initial complement of a hydrogen peroxide and a fault sodium carbonate — oxygen gas — the same — the mol of transition metals — a number — receiving — it can specify — the mol of transition metals — a number — receiving — usually — oxygen atom criteria — a 0.1 to 100 time mol — the hydrogen peroxide or fault sodium carbonate of a mol is used 0.1 to 10 times preferably. In addition, even if it uses oxygen / nitrogen mixed gas, an above-mentioned hydrogen peroxide, and an above-mentioned fault sodium carbonate independently, and uses together and uses them, they are not cared about.

[4] The acrylic polymer manufactured according to an atomic migration radical polymerization about halogen radical removal, functional-group conversion, etc. (meta) has labile radicals, such as a halogen, at the end. A halogen radical causes coloring or causes problems, such as deterioration of the quality of the product by generating of a free acid etc., and corrosion of a facility, in many cases. Then, desorbing a halogen with heating is mentioned as the approach of the dehalogenation of an acrylic (meta) polymer. Although an elevated temperature is desirable as a processing temperature, 120 degrees C or more 250 degrees C or less 140 degrees C or more 250 degrees C or less are 250 degrees C or less about 190 degrees C especially preferably more preferably preferably as a processing temperature requirement. Especially the processing time is not limited but can be heat-treated in dozens of hours from several minutes. Moreover, the time amount which processing takes can be shortened by making processing temperature high.

[0068] Furthermore, generally an acrylic-acid (meta) system (**) polymer can control polymer degradation by heating under antioxidant existence to the top where thermal resistance is high. Moreover, especially the existence of a solvent is not limited.

[0070] Furthermore, although especially the processing pressure force is not limited, 100 or less Torrs are 10 or less Torrs especially preferably 20 or less Torrs more preferably preferably [the heat-treatment under reduced pressure is desirable, and]. Since it is easy to influence of renewal of a front face in processing carrying out heating under reduced pressure, it is desirable to process in the state of the good renewal of a front face by stirring etc.

[0071]

[Example] Although a concrete example is shown below, this invention is not limited to the following example. The "weight section" and "% of the weight" are expressed the "section" and " %" among the following example and the example of a comparison, respectively. (Molecular-weight-distribution measurement) "Number average molecular weight" and "molecular weight distribution (ratio of weight average molecular weight and number average molecular weight)" were computed among the following example by the standard polystyrene converting method for having used gel permeation chromatography (GPC). However, chloroform was used as what was filled up with polystyrene bridge formation gel as a GPC column (shodex GPCX-804; Showa Denko K.K. make), and a GPC solvent.

[0072] In addition, this example and the example of a comparison are mainly estimating the thermal stability of a polymer with extent of change of the molecular weight distribution heat-treatment before and after heat-treatment. If a polymer deteriorates by a dimerization reaction etc., the molecular weight of a polymer stops gathering, and the value of molecular weight distribution will become large as a result.

(Example 1 of manufacture)

(Polymerization of acrylic-acid n-butyl, an ethyl acrylate, and acrylic-acid 2-methoxy ethyl) CuBr (4.6 sections) and an acetonitrile (41.6 sections) were added to the reaction vessel with an agitator, and it stirred for 15 minutes at 65 degrees C under nitrogen-gas-atmosphere mind. Acrylic ester (100 sections) (the items are acrylic-acid n-butyl (27.6 sections), ethyl-acrylate (39.8 sections), and acrylic-acid 2-methoxy ethyl (32.8 sections)), 2, and 5-dibromo adipic-acid diethyl (13.0 sections) was added to this, and stirring mixing was improved. Pentamethyl diethylenetriamine (triamine is called henceforth) (0.09 sections) was added, and the

aluminum silicate, an inorganic system adsorbent like a magnesium oxide, and inorganic powder in an acrylic (meta) polymer solution to reduce the amount of transition metal complexes in an acrylic (meta) polymer solution. An inorganic system adsorbent and inorganic powder not only act as a condensation nucleus of the transition metal complex which insolubilized, but can expect a physical and chemical absorption. The thing which uses aluminum, magnesium, silicon, etc. as a principal component and which combined independent or these is one of typical things of an inorganic system adsorbent, for example, silicon dioxide: — magnesium-oxide: — silica gel: — the zeolite system adsorbent; dawsonite compound; hydrotalcite compound named generically by water aluminosilicate mineral groups, such as clay system adsorbent; aluminum silicate sodium, such as silica alumina, aluminum silicate; activated-alumina; acid clay, and activated clay, is illustrated.

[0062] Some silicon of a silicic acid was permuted by aluminum, and, as for aluminum silicate, a pumice, fly ash, a kaolin, a bentonite, the activated clay, diatomaceous earth, etc. are known. Also in this specific surface area is also large and composite aluminum silicate has the high adsorption capacity force. Although KYO WORD 700 series (product made from consonance chemistry) etc. is mentioned as synthetic aluminum silicate, it is not necessarily limited to these.

[0063] A hydrotalcite compound some hydroxyl groups of the water hydroxide of divalent metals (Mg²⁺, Mn²⁺, Fe²⁺, Co²⁺, Cu²⁺, Zn²⁺, etc.) and trivalent metals (aluminum³⁺, Fe³⁺, Cr³⁺, Co³⁺, In³⁺, etc.), or said hydroxido a halogen — it exchanges for anions, such as to (DP N=0012) N, NO³⁻, CO³⁻, SO⁴⁻, Fe(CN)⁶³⁻, CH₃CO²⁻, an oxalate ion and salicylic-acid ion. Although the hydrotalcite thing which a divalent metal is Mg²⁺, and a trivalent metal is aluminum³⁺, and exchanged some hydroxyl groups for CO³²⁻ among these is desirable, for example, KYO WORD 500 series and KYO WORD 1000 series (all are the products made from Consonance Chemistry) are mentioned as synthetic compounds, it is not necessarily limited to these. Moreover, the adsorbent which calcinates the above-mentioned hydrotalcites and is obtained is also used suitably. Although the MgO-AlO₃ system solid solution which calcinates the hydrotalcites whose divalent metal is Mg²⁺, and whose trivalent metal is aluminum³⁺, and is obtained also in it is desirable, for example, KYO WORD 2000 (product made from Consonance Chemistry) is mentioned, it is not necessarily limited to these. In this invention it classifies as hydrotalcites also about the burned product of hydrotalcites. The adsorbent illustrated above may be used alone, or may mix and use plurality.

[0064] Moreover, although the amount of the adsorbent used is 0.1 - 10 weight section to the acrylic (meta) polymer 100 weight section, it is usually desirable that it is 0.1 - 5 weight section from economical efficiency and an actuation side.

[3] In the supply purification process of oxygen, it is also effective to supply oxygen at the time of heating of an acrylic (meta) polymer solution. A transition metal complex tends [comparatively] to oxidize, and generally, if a transition metal complex oxidizes, the solubility over a solvent will fall. Therefore, an acrylic polymer with more few (meta) impurities can be obtained by supplying oxygen with heating of the aforementioned polymer solution and addition of an adsorbent.

[0065] Mixed gas with the inert gas represented as a source of oxygen by the nitrogen which adjusted the oxygen density suitably besides air can be used. In this case, although oxygen will be mixed with an organic solvent, safety is securable by holding down an oxygen density to below the explosion limit. In addition to this as a source of oxygen of this invention, a peroxide like a hydrogen peroxide and a fault sodium carbonate is usable similarly.

[0066] the initial complement of oxygen — the mol of the transition metals for oxidation — a number — receiving — it can specify — the mol of transition metals — a number — receiving — usually — oxygen atom criteria — a 0.01 to 5000 time mol — desirable — a 0.1 to 10 time mol — the oxygen of a mol is used 0.1 to 5 times more preferably.

[0067] As the oxygen supply approach, there is the approach of filling up the gaseous-phase section of a mixing vessel in the example of mixed gas with nitrogen at the time of polymer solution heating. In this case, although it may be difficult to supply the amount of need oxygen by one restoration actuation, it is possible to permute mixed gas suitably in such a case, to

polymerization was made to start. Acrylic ester (400 sections) (the items are acrylic-acid n-butyl (111 sections), an ethyl acrylate (159 sections), and acrylic-acid 2-methoxy ethyl (130 sections)) was dropped continuously, carrying out heating stirring at 70 degrees C. Division addition of the triamine (0.04 sections) was carried out in the middle of dropping of acrylic ester. (Meta) When monomer conversion reached to 96%, after devolatilizing a ** monomer and an acetonitrile at 80 degrees C, 1, 7-OKUTA diene (119 sections), an acetonitrile (125 sections), and triamine (1.87 sections) were added, heating stirring was exceedingly carried out at 70 degrees C, and the polymer solution [1] which has an alkenyl radical was obtained (alkenyl radical installation reaction to an acrylic polymer). The solution containing an alkenyl radical and polymer (polymer [1]) was obtained by carrying out the little sampling of some polymer solutions, adding and diluting 3 times as many tovens as this with a volume ratio to a polymer solution, and carrying out solid content a ** exception. For a polymer [1], number average molecular weight is 111 about the number of average alkenyl radicals with which 17596 and molecular weight distribution are 1.11, and were introduced into per polymer 1 molecule by GPC measurement (polystyrene conversion). They were 2.07 pieces when asked by NMR analysis.

(Example 2 of manufacture)

(Polymerization of acrylic-acid n-butyl, an ethyl acrylate, and acrylic-acid 2-methoxy ethyl) CuBr (4.6 sections) and an acetonitrile (41.6 sections) were added to the reaction vessel with an agitator, and it stirred for 15 minutes at 65 degrees C under nitrogen-gas-atmosphere mind. Acrylic ester (100 sections) (the items are acrylic-acid n-butyl (27.6 sections), ethyl-acrylate (39.8 sections), and acrylic-acid 2-methoxy ethyl (32.8 sections)), 2, and 5-dibromo adipic-acid diethyl (13.0 sections) was added to this, and stirring mixing was improved. Pentamethyl diethylenetriamine (triamine is called henceforth) (0.09 sections) was added, and the polymerization was made to start. Acrylic ester (400 sections) (the items are acrylic-acid n-butyl (111 sections), an ethyl acrylate (159 sections), and acrylic-acid 2-methoxy ethyl (130 sections)) was dropped continuously, carrying out heating stirring at 70 degrees C. Division addition of the triamine (0.04 sections) was carried out in the middle of dropping of acrylic ester. (Meta) When monomer conversion reached to 96%, after devolatilizing a ** monomer and an acetonitrile at 80 degrees C, 1, 7-OKUTA diene (119 sections), an acetonitrile (125 sections), and triamine (1.87 sections) were added, heating stirring was exceedingly carried out at 70 degrees C, and the mixture which has an alkenyl radical was obtained (alkenyl radical installation reaction to an acrylic polymer).

(Rough *** removal of a polymerization catalyst) Heating devolatilization of the acetonitrile in mixture, unreacted 1, and the 7-OKUTA diene was carried out, and the remaining polymer solution was diluted with toluene. The solution which an insoluble polymerization catalyst is made to sediment with a centrifugal separator, removes, and contains an alkenyl end polymer (polymer [2]) was obtained. The adsorbent 4 section (KYO WORD 500 SH 2 section / KYO WORD 700SL 2 section : both product made from Consonance Chemistry) was added to the toluene solution of a polymer [2] to the polymer [2] of the 100 sections, and heating stirring was carried out under oxygen and a nitrogen mixed-gas ambient atmosphere. Insoluble matter was removed and the polymer (polymer [2]) which has an alkenyl radical by condensing a polymer solution was obtained, then — obtaining — having had — a polymer — [— two — ' —] — 180 — degree C — 12 — an hour — stirring — while — heating — devolatilization (whenever [reduced pressure] 10 or less torr) — having carried out — a thing — [— a polymer — [— two — ' —] —] — having obtained. The number average molecular weight of a polymer [2] was 16962, and molecular weight distribution were 1.15. The number of the alkenyl radicals introduced into per polymer 1 molecule was 1.6.

(Example 1) Acetonitrile [in a polymer solution [1]], 1, and 7-OKUTA diene was evaporated by carrying out devolatilization processing of the polymer solution [1] obtained in the example 1 of manufacture at 100 degrees C under a vacuum condition. Then, it is 0.05 weight ***** to a polymer about IRUGA NOX 1010 (Ciba-Geigy Japan make) as an anti-oxidant after dissolving this polymer with the toluene of that same weight and performing pressure filtration under pressure 1 kgf/cm². Furthermore, KYO WORD 500SH (product made from consonance chemistry) and KYO WORD 700SL (product made from consonance chemistry) were respectively

stirred in the 1000mL autoclave to the polymer for 2 weight %, the processing temperature of 150 degrees C, and processing-time 4 hours as an adsorbent. Then, it cooled radiationally until it became a room temperature, and the acrylic (meta) polymer was obtained from the founding liquid which may have had pressure filtration performed under pressure 1 kgf/cm² by distilling off toluene. As a result of performing GPC measurement (polystyrene conversion) to the obtained polymer, number average molecular weight was 17572 and molecular weight distribution were 1.14. A result is shown in Table 1.

(Example 2) Acetonitrile [in a polymer solution [1]], 1, and 7-OKUTA diene was evaporated by carrying out devolatilization processing of the polymer solution [1] obtained in the example 1 of manufacture at 100 degrees C under a vacuum condition. Then, it is 0.05 weight %, to a polymer about IRUGA NOx 1010 (Ciba-Geigy Japan make) as an anti-oxidant after dissolving this polymer with the volume of that same weight and performing pressure filtration under pressure 1 kgf/cm². Furthermore, KYO WORD 500SH (product made from consonance chemistry) and KYO WORD 700SL (product made from consonance chemistry) were respectively stirred in the 1000mL autoclave to the polymer for 2 weight %, the processing temperature of 180 degrees C, and processing-time 4 hours as an adsorbent. Then, it cooled radiationally until it became a room temperature, and the acrylic (meta) polymer was obtained from the founding liquid which may have had pressure filtration performed under pressure 1 kgf/cm² by distilling off toluene. As a result of performing GPC measurement (polystyrene conversion) to the obtained polymer, number average molecular weight was 17279 and molecular weight distribution were 1.15. A result is shown in Table 1.

(Example 1 of a comparison) Seven weight sections and KYO WORD 700SL (product made from consonance chemistry) were stirred in the 100mL autoclave to the polymer for 3 weight %, the processing temperature of 150 degrees C, and processing-time 5 hours to the polymer [2'] of the 100 sections obtained in the example 2 of manufacture in KYO WORD 500SH (product made from consonance chemistry) as an adsorbent. Then, after having cooled radiationally until it became a room temperature, and making it dissolve in toluene, the acrylic (meta) polymer was obtained by distilling toluene out of the founding liquid which might be removed in insoluble matter. As a result of performing GPC measurement (polystyrene conversion) to the obtained polymer, number average molecular weight was 20943 and molecular weight distribution were 1.75. A result is shown in Table 1.

(Example 2 of a comparison) Three weight sections and KYO WORD 700SL (product made from consonance chemistry) were stirred in the 100mL autoclave to the polymer for 10 weight %, the processing temperature of 150 degrees C, and processing-time 5 hours to the polymer [2'] of the 100 sections obtained in the example 2 of manufacture in KYO WORD 500SH (product made from consonance chemistry) as an adsorbent. Then, after having cooled radiationally until it became a room temperature, and making it dissolve in toluene, the acrylic (meta) polymer was obtained by distilling toluene out of the founding liquid which might be removed in insoluble matter. As a result of performing GPC measurement (polystyrene conversion) to the obtained polymer, number average molecular weight was 25694 and molecular weight distribution were 2.98. A result is shown in Table 1.

[0073]

[Table 1]

重合体	処理条件						分子量分布
	熱処理時間 時間	溶媒の量 kg	溶媒の量 (KYO500/700)	温度 度	時間 時間	時間 時間	
重合体1 重合体2	2.5	50L	2/2	150	4hr	全量	1.15
重合体1 重合体2	2.5	50L	2/2	150	5hr	全量	1.15
重合体1 重合体2	2.5	50L	2/2	150	5hr	全量	1.15
重合体1 重合体2	2.5	50L	2/2	150	5hr	全量	1.15
重合体1 重合体2	2.5	50L	2/2	150	5hr	全量	1.15

* 重合量は、重合体の重量を100重量としたときの値を記載。

The number average molecular weight and molecular weight distribution of a polymer of examples 1 and 2 were close to the polymer before heat-treatment [a polymer [2']]. On the other hand, the polymer of the examples 1 and 2 of a comparison became number average molecular weight

and a value with big molecular weight distribution. When an antioxidant exists shows that thermal stability improves.

(Example 3) It is 1 weight %, about IRUGA NOx 1010 (Ciba-Geigy Japan make) as an anti-oxidant to the polymer [2'] of the 100 sections obtained in the example 2 of manufacture. Three weight sections and KYO WORD 700SL (product made from consonance chemistry) were stirred in the 100mL autoclave to the polymer for 10 weight %, the processing temperature of 150 degrees C, and processing-time 5 hours in KYO WORD 500SH (product made from consonance chemistry) as an adsorbent. Then, after having cooled radiationally until it became a room temperature, and making it dissolve in toluene, the acrylic (meta) polymer was obtained by distilling toluene out of the founding liquid which might be removed in insoluble matter. As a result of performing GPC measurement (polystyrene conversion) to the obtained polymer, number average molecular weight was 16858 and molecular weight distribution were 1.18. A result is shown in Table 2.

(Example 3 of a comparison) Five weight sections and KYO WORD 700SL (product made from consonance chemistry) were stirred in the 100mL autoclave to the polymer for 5 weight %, the processing temperature of 150 degrees C, and processing-time 5 hours to the polymer [2'] of the 100 sections obtained in the example 2 of manufacture in KYO WORD 500SH (product made from consonance chemistry) as an adsorbent. Then, after having cooled radiationally until it became a room temperature, and making it dissolve in toluene, the acrylic (meta) polymer was obtained by distilling toluene out of the founding liquid which might be removed in insoluble matter. As a result of performing GPC measurement (polystyrene conversion) to the obtained polymer, number average molecular weight was 24742 and molecular weight distribution were 2.58. A result is shown in Table 2.

(Example 4 of a comparison) It stirred in the 500mL eggplant flask under air to the polymer [2'] obtained in the example 2 of manufacture for the processing temperature of 170 degrees C, and processing-time 3 hours. As a result of performing GPC measurement (polystyrene conversion) to the obtained polymer, molecular weight distribution were 3.29. A result is shown in Table 2.

[0074]

[Table 2]

重合体	処理条件						分子量分布
	熱処理時間 時間	溶媒の量 kg	溶媒の量 (KYO500/700)	温度 度	時間 時間	時間 時間	
重合体3 重合体4	2.5	50L	3/10	150	5hr	全量	1.18
重合体3 重合体4	2.5	50L	3/10	150	5hr	全量	2.58
重合体3 重合体4	2.5	50L	3/10	150	5hr	全量	3.29

* 热处理量は、重合体の重量を100重量としたときの値を記載。

In the examples 2, 3, and 4 of a comparison, existence of an antioxidant controlled molecular weight distribution or less to 1.5 in the example 3 in the same conditions by adding heating and an adsorbent to a polymer to increasing, so that thermal stability cannot be held but molecular weight distribution exceed 1.5.

[0075]

[Effect of the Invention] According to this invention, thermal and oxidation degradation can be controlled for processing of the acrylic system polymer manufactured using an atomic migration radical polymerization (meta), and simple processing can be performed.

[Translation done.]